

Surface Free Energy as a Function of Size and Shape of Nanocrystal

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A method for the analytical calculation of the surface free energy of nanocrystals (which consist of N atoms) was proposed. Nanocrystals (NC) have the shape of a rectangular parallelepiped with a square base. The ratio (f) of the side edge length to the length of basis edge is defined the shape of system: $f = 1$ for cubic; $f < 1$ for platelike; $f > 1$ for rodlike shapes. Considering only the interactions between the nearest neighbours, and using an Einstein model (for vibrations of atoms into lattice), we have the expression for surface free energy (σ) per atom of NC as follows

$$\sigma(N, f) = [L / 3 c^2 \tilde{n} [k_b \Theta(N, f) / 2 c^2 k_n^*(N, f)] (0.5 + \{ \exp[\Theta(N, f) / T] \tilde{n}^1 \}) k_y(S)] .$$

Here $L \tilde{n}$ is the sublimation energy (per atom) of macrocrystal; $k_b \tilde{n}$ is the Boltzmann constant; $c \tilde{n}$ is the distance between the centers of neighbouring atoms in NC (for the "vacansionalless" approximation): $c = (V/N \alpha_n)^{1/3}$; $V \tilde{n}$ is the volume of NC; $\alpha_n = \pi / 6 k_y$, $k_y \tilde{n}$ is the coefficient of atoms packing in structure of crystal; $k_y(S) \tilde{n}$ is the packing coefficient for the surface layer: $k_y(S) \equiv k_y^{2/3}$;

$$k_n^*(N, f) = k_n(N, f) / k_n = 1 \tilde{n} (\alpha_n / f)^{2/3} (2f + 1) / (3 N^{1/3}) ,$$

where $k_n(N, f) \tilde{n}$ is the average (on all atoms of NC) first coordination number into NC; $k_n \tilde{n}$ is the first coordination number into bulk of macrocrystal.

The dependence of the Einstein temperature via the size and via the shape NC (for substances where the energy of "zero-point oscillations" smaller than the chemical binding energy) has the form: $\Theta(N, f) \equiv \Theta(N=\infty) [k_n^*(N, f)]^{1/2}$, where $\Theta(N=\infty) \tilde{n}$ is the Einstein temperature of the macrocrystal.

The calculations permit one to draw the following conclusions:

1. The dependence $\sigma(T)$ decreases as T increases. It more visible when the value N is smaller (at the same f), or when the divergence value f from unity is larger (at the same N).
2. The dependence $\sigma(N)$ decreases as N decreases. It is more visible when the value T is larger (at the same f), or when the divergence value f from unity is larger (at the same T).
3. The large divergence of the system's shape from equilibrium (i.e. cubic) shape the more visible the decrease of function $\sigma(T, N)$ at the increase of T , or at the decrease of N .
4. At "magic number" of atoms (N_m) into NC (when can build cubic NC without defects, where $f = 1$) the functions $k_n^*(N)$, $\Theta(N)$ and $\sigma(N)$ have local maximum. It leads to the appearance of a set of maximums on the dependencies at the values of "magic numbers" ($N_{m1} > N_{m2} > N_{m3} > \dots$).
5. Since we have: $\sigma(N \neq N_m, f \neq 1) < \sigma(N_m, f = 1)$, then NC with nonequilibrium (i.e. noncubic) shape was more easy to stick to surface (or to other NC) than NC with the more thermodynamically stable (i.e. cubic) shape of surface.

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